ORIGIN OF WEAK FERROMAGNETISM IN RARE-EARTH ORTHOFERRITES

R. M. Bozorth
Bell Telephone Laboratories,
Murray Hill, New Jersey
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Weak ferromagnetism, with a ferromagnetic moment of n_B = 0.03 to 0.1 Bohr magneton per molecule, has been observed[1-3] in the rare-earth orthoferrites, $MFeO_3$, where M = Sm(62) to Lu(71), inclusive. In all of these n_B depends only slightly on temperature between 100 and 300°K, and in all single crystals examined[2,3] except in $SmFeO_3$ the magnetization is along the orthorhombic c axis in this temperature range.

It is known from the neutron diffraction work of Koehler, Wollan, Wilkinson, and Cable[4] that at these temperatures the moments of the Fe^{3+} ions in $HoFeO_3$ and $ErFeO_3$ are ordered so that each ion has 6 nearest neighbors of opposite moment (their[5] type G), all aligned nearly parallel to the a axis.

This note is to show that the direction of the weak ferromagnetism is a result of the disturbing effect of the crystal field on the much stronger exchange field. The known orthorhombic crystal structure, worked out by Geller,[6] determines the effect of the disturbing crystal field on the array of Fe^{3+} moments, the directions of which are determined approximately by neutron diffraction. A similar explanation of the weak ferromagnetism of αFe_2O_3 and of some fluorides has been proposed by Dzialoshinskii.[7,8]

Consider one of the Fe^{3+} ions in Fig. 1, its magnetic moment directed along the a axis by exchange interaction as shown by the arrow, and let the crystal field lie along an arbitrary direction represented by the broken line (not in the plane of the paper). Then the ion moment will be turned slightly by the crystal field away from its exchange position, so that it will have components parallel to the b and c axes. Consideration of these components for the 4 appropriate ions shows that the net component of all of the ions is parallel to the c axis. The directions of the crystal field acting on these 4 ions is determined by the symmetry of the crystal, represented by the orthorhombic space group $Pbnm$ (D_{2h}^{16}) which has a reflecting plane $\perp c$ and a screw axis $\| a$ (see Fig. 1) as well as other symmetry elements.

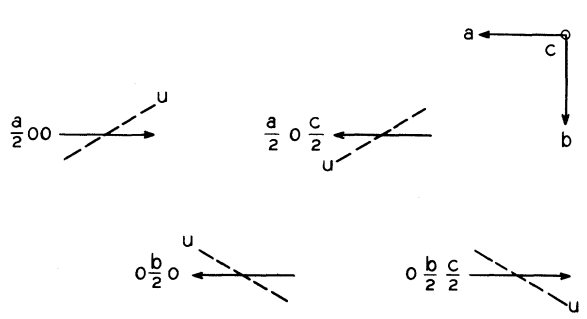

FIG. 1. Arrows represent directions of magnetic moments in 4 representative Fe^{3+} ions in $MFeO_3$, as they would be held by exchange forces alone; broken lines represent (arbitrary) directions of the crystal field. The letter u indicates the end of the line that is above the plane of the paper and has a component along the positive c axis. Coordinates of atoms are given in units of crystal cell dimensions.

Since the moment of the Fe^{3+} ion is about M = 5 Bohr magnetons, the experimentally determined moment of the crystal corresponds to a deviation of the direction of M from the a axis by 2 to 5°. This indicates that the crystal field is much weaker than the exchange field, in agreement with accepted ideas.

The behavior of $SmFeO_3$ is exceptional[3] among the orthoferrites in that the weak ferromagnetism lies along the a axis. An analysis similar to that given above shows that this is to be expected if the exchange forces act to align the Fe^{3+} moments along the c axis (see Table I). Unfortunately a test of this alignment in $SmFeO_3$ with neutron diffraction is difficult because the

Table I. Direction of weak spontaneous magnetization, σ_0, as dependent on type[a] of ordering and approximate direction of Fe^{3+} moments.

Type	Approximate moment axis	Direction of σ_0
G	a	c
	b	$\sigma_0 = 0$
	c	a
A	a	$\sigma_0 = 0$
	b	c
	c	b
C	a	b
	b	a
	c	$\sigma_0 = 0$

[a]See reference 5.

nuclear cross section of Sm is so high. At higher temperatures the ferromagnetism lies along the c axis[3] as in the other orthoferrites at room temperature.

At temperatures below 20°K the moments of the rare-earth ions begin to be ordered. Then the exchange interaction with these ions has an important influence on the magnetic properties of the crystal, and the spontaneous magnetization is sometimes larger by orders of magnitude; under these conditions the assumptions used above no longer apply and the magnetization is no longer weak.

The directions of spontaneous magnetization have also been determined for two other types of ordering of moments, namely types A and C according to the nomenclature of Wollan and Koehler.[5] Results for all three types, with given spin directions, are given in Table I. The possibility of generalizing the method of calculation has been discussed with Professor W. H. Zachariasen.

The author is indebted to Dr. Elizabeth A. Wood and Dr. S. Geller for discussions concerning the crystal symmetry of the orthoferrites, and to Dr. W. C. Koehler of Oak Ridge National Laboratory for a discussion of the results of neutron diffraction. All of the work on single crystals of the rare-earth orthoferrites has been made possible by the growth of large crystals by Remeika.[9]

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HEAT CAPACITY OF SUPERCONDUCTING ZINC

Norman E. Phillips
Department of Chemistry and Radiation Laboratory,
University of California,
Berkeley, California

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Zinc provides an interesting example for the study of the electronic heat capacity of superconductors because it shows the sharp transition characteristic of the ideal superconducting state and at the same time the lattice heat capacity is relatively small, amounting to only 3% of the total at temperatures just below the transition temperature. This report describes the results of measurements on superconducting and normal zinc between 0.15° and 1.1°K.

Temperatures below 1°K were obtained by the adiabatic demagnetization of copper potassium sulfate. This salt was chosen in the belief that its susceptibility follows a Curie-Weiss law to 0.1°K.[1,2] The zinc sample was connected to the salt pill through a superconducting heat switch and a mechanical heat switch was used to provide thermal contact between the salt and a helium vapor pressure bulb. A carbon resistance thermometer attached to the sample was calibrated against the mutual inductance of a set of coils surrounding the salt pill and the mutual inductance, M, was in turn calibrated against the temperature, T, calculated on the Leiden 1955 scale. Temperatures below 1°K were calculated from the relation

$$M = A + B/(T - \Delta), \qquad (1)$$

in which the constants, A, B, and Δ were determined by plotting M vs $(T - \Delta)^{-1}$ for temperatures between 1.1° and 4.2°K and for various values of Δ. The best straight-line fit was obtained for $\Delta = 0.033°$ and this value was used in the calculations. A more detailed account of the experimental method has been given in connection with measurements on copper and aluminum.[3]

The sample used was a single crystal of 99.999% zinc grown in a helium atmosphere and showing a sharp superconducting transition. A warming curve taken through the transition region at a constant rate of heat input changed slope by a factor of 2.3 ± 0.1 within a temperature interval of 0.001° at 0.825°K. The discontinuity in heat capacity estimated by extrapolation of measured heat capacity points to 0.825°